

*Did not have capability or experience*

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

SUBJECT: Analysis of Llangollen Landfill Sample

DATE: May 9, 1977

TO: T. O. Munson, Ph.D.  
Chief, Organic Analysis Unit

TO: Orterio Villa, Jr.  
Director, AFO

cc: Monitoring  
Andrew  
File 5/11/77  
Montgomery

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This memo contains a description of the work performed related to the Llangollen Landfill problem from the initial preparations for sample collection through a discussion of the analytical results. At this time, the results have not yet been received from the University of Illinois group (Dr. Ed Chian).

I. Introduction

We were requested to collect and analyze for trace organics by GC/MS samples from monitoring, recovery, and drinking water wells specified by the Water Supply and Enforcement Branches. The data were to be used to determine whether organic chemicals from the Llangollen Landfill were present in water supply wells as far from the landfill as Well #2 of the Artesian Water Company and Well PW-3 of the Amoco Chemical Corporation (see attached sketch).

*See Appendix*  
We recognized that this request would be straining our analytical capabilities in two areas:

1. Detection Limit -- the toxic limits for many chemicals in drinking water are below the limits of detection by our GC/MS system; and,
2. Volatile Organics -- many of the chemicals of interest would probably be volatile organics because of their mobility in aquatic systems, and our capabilities and experience for volatile organics analysis by GC/MS are quite limited.

As will be described in the next section, efforts were made to strengthen the analysis program in these areas.

II. Sample Collection

Although personnel at AFO planned and prepared for the sample collection trip over a period of several months, things got a bit hectic when we were informed ten days prior to the sampling date that samples were to be collected for Dr. Ed Chian of the University of Illinois as well.

*Never Stated at time of Request or shortly thereafter*

*had at least 10-15 days delay*

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At the sample site, another difficulty was encountered. Due to the soggy soil and roughness of the terrain, neither Well 49 nor alternate choice Well 24 could be sampled. Samples were obtained from six wells -- Monitoring Wells, 43, 27, and 29; Recovery Well 3; Artesian Water Company Well 2; and Amoco Chemical Corporation Well PW-3.

1. AFO Samples. The primary samples were 1-gallon grab samples to be analyzed for extractable organics. We took 1-liter samples for volatile organics analysis by the hexadecane extraction procedure which is used routinely by EPA, Region II. Although our experience using this procedure for GC/MS was quite limited, the method had been well documented by Region II. We attempted to improve our detection limit for extractable organics by passing larger volumes of water through XAD-2 resin columns to concentrate the organic materials. Although our experience with this method was also quite limited, a preliminary field test at several of the Llano wells on 2/1/77 by J. Barron produced apparently acceptable samples.

2. Dr. Ed Chian's Samples. At the time of sampling, we thought we had collected nearly exactly the samples which had been requested by Dr. Chian -- a volatile organics sample in a 40 ml bottle with a teflon-faced septum and a 1-gal. sample for extractable organics in a glass bottle with a teflon-lined screw-cap. He asked that the 1-gal bottle be baked in a muffle furnace which we could not do, but under ordinary circumstances, a solvent rinsed bottle would have been sufficient. Unfortunately, somehow over the telephone we did not understand that Dr. Chian wanted three samples each for volatile organics. The last of the two additional samples required him to use water from the 1-gal. samples for volatiles analysis. In this case, the residual solvent in the bottles did cause him some problems.

### III. Sample Analysis

1. Extractable Organics. A portion (1 liter) of each of the six samples was solventily extracted to yield acids, bases, and neutrals fractions -- giving 18 samples to be run by GC/MS. The extracts were concentrated down to about 1 ml with the final solvent being benzene. The concentration process results in the loss of most volatile organics (such as acetone and toluene).

2. XAD-2 Resin Samples. The solvent used to extract the adsorbed organic material from the column is also concentrated -- once again one would expect to lose most of the volatile organics. These samples proved to be useless even though the test samples run earlier had looked good. The reagent blank (extract from a column which had not had water run through it) had many organic chemicals of high concentration which made the GC/MS runs of the sample extracts uninterpretable.

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3. Hexadecane Volatile Organics Extracts. We followed the method quite carefully but still came up with uninterpretable results. Even though we bought the exact grade and brand of hexadecane as specified in the method, the hexadecane itself contained so many peaks of contributing material that the extracts were useless.

#### IV. Results and Discussion

The enclosed table summarizes the results of the GC/MS scans of the 18 sub-fractions of the 6 samples. The peak number is an arbitrary designation roughly corresponding to the elution order of the peaks. The base peak represents the molecular weight (usually -- actually, charge-to-mass ratio) of the most abundant mass fragment in each mass spectrum. The purpose of the table is to provide an illustration of the similarities between the various samples. An "X" in a row denotes the presence of that compound in that sample fraction (a dotted "X" indicates that the match is not perfect), a blank space denotes the absence of that compound in that sample fraction, and an "O" in the first line of a column indicates that no peaks at all were seen in that sample fraction.

Rather surprisingly, W2 showed three large peaks and one smaller one -- not what one would hope to find in a drinking water well. Upon subsequent analysis of the remaining samples an event worthy of note occurred.

The acids fraction of W27 was inadvertently checked off as having been run. Upon completion of the samples, only the Amoco PW3 was found to have the peaks present in the Artesian W2. Examination of the attached sketch map shows the dilemma -- the two wells furthest from each other and furthest from the landfill had similar contamination but no relation to the landfill. At this point, under mild duress, I communicated some "preliminary results" to the Regional Office. Shortly thereafter, during the preparation of this report, the omission was discovered and the acids fraction of W27 analyzed.

One can see from the Table that the contamination patterns found in the three wells (Artesian 2, Amoco PW3, and PW27) are clearly related. All four of the compounds present in W2 are also in PW27 and in PW3. Seven of the thirteen compounds present in PW3 are also present in PW27. These results suggest that chemicals are migrating from the landfill into Artesian Well 2 and Amoco PW3.

The computerized mass spectral search system lead to the tentative identification of two of the four peaks found in Artesian W2. The first peak matched chlorocyclohexanol and the second peak matched dichlorocyclohexanol. One of the peaks in PW3 appears to be dichlorotoluene.

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One of the other peaks in W2 appears to be chlorinated (based upon the isotope ratio of the mass fragments) and five of the remaining peaks in W3 appear to be chlorinated.

The contamination in the other three wells sampled did not seem related to the three wells discussed above. From the table, one can see that no contaminants were detected in MW42 and only one peak in MW3. Ten large peaks were detected by the GC/MS scan of the sample from MW29. Several of the peaks were tentatively identified (dinonyl phthalate, tributyl phosphate, a substituted phenol) but probably are not of too much interest because they do not occur in the other samples.

An important point to mention here is that, in order for a compound to be detected by our GC/MS system run as it was for these scans, the concentration in the original 1-liter sample would have to be on the order of 50 ug/l or 50 parts-per-billion. One can see that many chemicals which are alarming at the 5 to 10 ppb level in drinking water could have been present and passed undetected.

Although we do not have standards of the chlorinated materials identified in the drinking water and therefore can not quantitate them, one can say that, judging from the sizes of the peaks observed, the levels could be 1 ppm or greater.

In conclusion, a few comments are probably appropriate about how our results compare to those of Ron Webb from EPA Athens (analyses performed in 1974).

Webb analyzed samples from three of the wells which were sampled this time -- W2, Artesian W2 and MW29. He did not find any compounds in W2. He did identify camphor, cresols, caprolactam, benzoic acid, and a lot of aliphatic acids in W2. Most of the materials he found were below the levels which we would have detected, so perhaps it is not too surprising that we detected only one peak. In W29, other than a suite of aliphatic acids, he detected chlorobenzene, p-dichlorobenzene, and triethyl phosphate. Of the ten major peaks which we detected, we identified dichlorobenzene, dinonyl phthalate and tributyl phosphate.

TOM/jr

cc: James W. Madsen

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